

Ion Exchange Resin Decomposition

(Extracted from the Diaion Manuals page 72 to 93)

[Table I-4-1] Performance Degradation and Functional Troubles of IERs

Breaking down: ⇒ IERs loss by flowing out during backwashing, Increase pressure loss, channeling → Poor effluent quality, Declined treatment capacity
Deposition of foreign materials: Cation exchange resins: Fe deposition, CaSO ₄ precipitation in regeneration by H ₂ SO ₄ Anion exchange resins: Polyvalent metal hydroxides, SiO ₂ gellation
Oxidation of SACERs: ⇒ Irreversible swelling with lower crosslinkage → Increase of moisture content and swelling → Decline of exchange capacity per volume (Better effluent quality due to less Na leakage in deionization) ⇒ elution of resins and PSA in lowering crosslinkage → Irreversible contamination of AERs → Worse effluent quality by leakage once fully contaminated
Oxidation of SBAERs: ⇒ Lowering functional groups, lowering basicity → decrease the moisture content, the degree of swelling, the total exchange capacity and the neutral salt splitting capacity and increase the exchange capacity of weakly basic groups → difficulty in rinse Lowering basicity decreases the exchange capacity toward weakly acidic components as SiO ₂ and HCO ₃ ⁻ ⇒ Dropping-outs of the exchange groups decrease the reaction rates and increase ion leakages
Organic contamination of AERs: ⇒ Ion exchange reaction rate declines → Total exchange capacity and Neutral salt splitting capacity decrease and weakly basic groups generate → Poorer rinse efficiency, worse effluent quality

4. Performance Degradation of IERs

Long-term use of IERs occasionally causes some operation troubles; declined treatment capacity or poor effluent quality. We must consider that such troubles might be caused the performance degradations of IERs themselves in these cases. Table I-4-1 summarizes such performance degradations and functional troubles.

(1) Physical Durability of IERs

IERs are apt to break into small particles to bring pressure drops in the columns and to increase the outflow during backwashing after having been recycled many times. Once IERs are broken in the mixed beds where CERs and AERs are packed in the same column, other problems than pressure drops sometimes occur: e.g., it becomes difficult to separate such two kinds of IERs in the prior process to the regeneration, or the broken CERs move up to the upper part of the columns and then contact with NaOH, a regenerant, to become in the Na-form and derive the increase of

Na-ion-leakage.

Such crushes are caused mainly by the distortion due to the volume changes accompanied swelling and/or contraction of IERs. We have already explained that the volumes of IERs usually vary in accordance with the increase/decrease of the moisture contents in IERs, sudden volume changes trigger off the distortion in the resin phase and bring the cracks or crushes at last. The cracks or crushes are accelerated when IERs receive physical impacts such as backwashing or mixing. The IERs with cracks inside are easy to be broken down, and the large particles tend to be broken down more easily than small ones.

The strength is one of the important properties of industrial-use IERs since they are used repetitiously. It is not, however, to examine their physical durability. There are some indirect methods for this purpose and they are useful to grasp the approximate trend of the IERs strength: 1) to observe the crushes with the impacts by a ball-mill or a shaker, 2) to measure the resistance load of the IER beads toward crushing, 3) to observe the lab-scale breakdowns after some repetition model operations. Care must be taken to use these methods because such observed results do not always agree with the trouble frequencies in the actual operations.

The physical durability of IERs is affected not only by the manufacturing technology of IERs but also by the design of the IER columns: i.e. the defects of column equipments sometimes accelerate such crushes. If the ratios of the height to the diameter of IER columns are too large, the IER volumes are inclined to increase suddenly and to have the resin beads at the bottom be pressed more heavily. These pressures may accelerate the breakdowns of IERs. Thus, the column design should be taken care of, in particular, when the concentration of regenerants is high and the low crosslinkage IERs are used.

The high crosslinkage IERs seem, by intuition, physically stronger than the low ones, but they are not always so strong. The high crosslinkage IERs have less elasticity instead of sufficient hardness, and the low crosslinkage ones, on the other hand, have less hardness instead of sufficient elasticity. As a result, the moderate crosslinkage IERs with well-balanced property are empirically preferable.

The physical strength of IERs decline by other reasons: chemical changes and foreign materials caused by organic contamination, sedimentation of metal hydroxides or freezing. SACERs often swell irreversibly, which we will explain later, and they become easy to be broken down by excess oxidation.

SBAERs are apt to adsorb some organic compounds irreversibly and to accumulate them inside or on the surface of the resin particles. Such accumulation that is called "organic contamination" makes SBAERs

vulnerable to breakdowns. CERs can be, in some particular cases, contaminated by organic compounds and be accelerated to be broken down as a consequence.

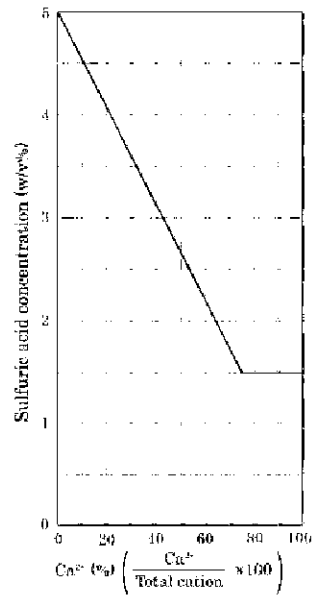
Porous-type IERs are superior to gel-type ones in physical durability, and the reason of this phenomenon is considered to be that the macropores inside of them play a role of shock adsorbers toward sudden volume changes.

(2) Interfere of ion-exchange by accumulated foreign materials

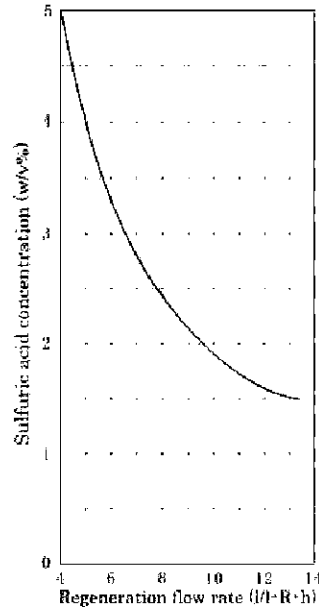
1) SACERs

When one passes influents with suspended matters through IER columns, the suspended matters accumulate in the resin layers. Backwashing, in these situations, must be done elaborately lest the accumulated matters may cause ion-exchangeability poor. As an example: in the long-term operations of the softening plants with CERs the accumulated Fe compounds usually increase the leakage of hard ions and decrease the ion-exchange capacity. NaCl solutions are preferably used as regenerants in the softening plants, Fe compounds gradually accumulate due to such NaCl solutions have poor potential to desorb Fe compounds. Thus, the Fe compounds in the influents must be removed preliminarily. If such accumulation happens unfortunately, one could wash the degraded IERs with HCl aqueous solutions to recover their performances. We call it "rejuvenation" to have the degraded IERs recover their original functions. We use the so-called iron-removal resurrection agents that are NaCl solutions with some organic acids or chelating agents as additives in case the equipment materials are not bearable against HCl solutions.

Other than suspended matters in influents, care must be taken of the precipitates in the resin layers. HCl solutions are generally used as regenerants to regenerate CERs to H-form. H₂SO₄ solutions could be used instead of HCl ones with no problems if the targeted CERs adsorb small amount of Ca²⁺ and Ba²⁺ ions. In ordinary water treatment plants, however, the CERs adsorb considerable amount of Ca²⁺ ions. If one uses H₂SO₄ solutions as regenerants in these cases, poorly soluble CaSO₄ are formed and precipitated to fill up the gaps in the resin layers and finally to shut down the flow in the worst cases. Thus, one should obey the so-called stepwise regeneration method in these cases. That is, one should use sufficiently diluted H₂SO₄ solutions at a high flow rate and then gradually increases the H₂SO₄ concentration at a decreased flow rate in accordance with the decline of Ca²⁺ ions in the resins. Figures I-4-1 and I-4-2 show the relevant data.



[Fig.I-4-1] Ca contents in influent vs. H_2SO_4 concentration



[Fig.I-4-2] H_2SO_4 concentration vs. Flow rates

The IERs with $CaSO_4$ precipitates inside could be rejuvenated by washing with HCl solutions. Another rejuvenation method consists of two steps: 1) be treated with NaCl solutions to exchange such metal ions with Na ions, 2) be regenerated with H_2SO_4 solutions. As for metal salts precipitates, one can remove them from IER columns in these ways, one must be careful in practical operations never to form such precipitates.

2) AERs

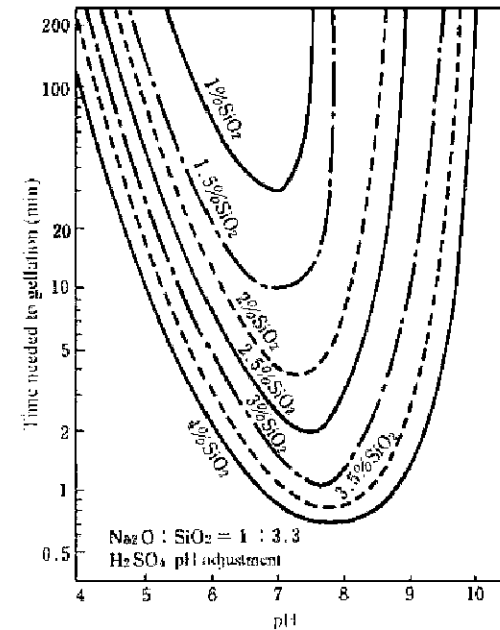
Since similar debris accumulation does sometimes occur in AERs columns and interfere ion-exchange operation, careful backwashing is also needed in AERs column. Furthermore, silica compounds, e.g. SiO_2 , often precipitate and decline AERs' removal function when such water treatments are done with SBAERs. Early and elaborate regenerations with relatively warm/hot NaOH solutions as regenerants are recommended in these cases.

Another notice in the washing process of AERs after regeneration is

that soft-water or H-water treated with H-form CERs. Must be used as washing water in order to avoid the precipitates of $Mg(OH)_2$ that often appear if one uses hard-water as washing waters.

In the cases where the content of SiO_2 in the influents is rather high, the SiO_2 captured inside of AERs might become too much to be dissolved and then might become in gel-form. Lest becoming into such gel-form, one must be careful in such gelation when the regeneration level is low particularly. Data regarding gelation of SiO_2 is illustrated in Fig.I-4-3.

In 4-bed 5-tower systems which include a WBAER column, special care is needed due to the fact that the spent regenerant from the SBAER downline is used to regenerate the WBAER. However, if this regenerant has a high concentration of SiO_2 , gelation of SiO_2 occurs in the resin layer and may even make it impossible to pass the fluid through the system. Thus, in this type of systems, any effluent fraction with a high concentration of SiO_2 should be discharged, and the WBAER regenerated by the spent regenerant with a low SiO_2 content.



[Fig.I-4-3] SiO_2 level vs. Time needed to gelation⁽¹⁰⁾

3) Mixed bed IERs

In the mixed bed IER systems, each CERs and AERs in the same columns are regenerate, as they are inside the columns, with their own regenerants respectively. In these cases, two kinds of regenerants contact at the layer that separates CERs from AERs and sometimes form some precipitates. One example of such precipitates is gel-form SiO_2 generated by contact of SiO_2 in AERs or in regeneration effluents with mineral acids or H-form IERs, and another example is metal hydroxides of Ca or Mg in CERs or regeneration effluents with NaOH or OH-form IERs.

(3) Oxidation and irreversible swelling of SACERs

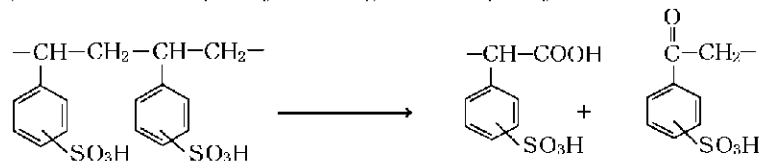
Oxidation of IERs is caused by oxidizing agents such as free chlorine, nitric acid or dissolved oxygen and accelerated by the co-existence of catalysts; Fe, Cu and other metals. Oxidation decreases the crosslinkage and the ion-exchange capacity per volume of IERs but increases the moisture content and degree of swelling. The decline in the crosslinkage brings the better regeneration efficiency and the decrease of Na leakage during deionization.

Polystyrenesulfonic acid (PSA) that elutes from IERs' main structures during such oxidation contaminates AERs irreversibly, and makes the effluent quality worse by its own leakage into it.

Styrene-type SACERs are chemically stable and resistant to high temperatures, 100 ~ 120 °C, but are somewhat oxidizable.

In oxidation of SACERs, the crosslinked resin matrix is mainly oxidized and the chain links in its network structure are broken. These breaks decrease the crosslinkage and cause the irreversible swelling as a result.

Low crosslinkage IERs are easy to be oxidized and to swell irreversibly. Regarding ion-exchange capacity of the oxidized IERs, the whole capacity does not decline since there are no changes in the functional groups, unless the resin matrix is broken down by vigorous oxidation, though the ion-exchange capacity per volume declines by the irreversible swelling due to oxidation. On the contrary, the actual decline of the crosslinkage sometimes causes better regeneration efficiency, that is, less leakage of Na, better effluent quality and larger flow capacity.



In water treatment, free chlorine of low level in the influent is one of the causes of irreversible swelling because it contacts IERs much for long terms though it is at a very low level. Furthermore, metal ions, e.g. Fe or Cu, work as catalysts in spite of their low levels, and accelerate the oxidation of IERs. Further oxidation breaks IERs and dissolves them within columns, and sometimes transforms the IER particles and makes it impossible to let influents flow as a result. Thus, one should remove such oxidative compounds from effluent as much as possible before the IER treatment.

Table I-4-2 summarize the results of the oxidation of CERs of three crosslinkages, 4%, 8% and 15%, by the electric current, 1A at 4V, in an electrolysis cell which 20% NaCl solution was included in. It shows the increasing moisture content and irreversible swelling in accordance with the oxidation process. Low crosslinkage IERs are easy to be oxidized and to swell irreversibly, as we have already explained.

[Table I-4-2] Oxidation of Cation Exchange Resins⁽¹¹⁾

Oxidation Time	CER of DVB 4%			CER of DVB 8%			CER of DVB 15%		
	Exchange Capacity	Neutral salt Splitting Capacity	Moisture content	Exchange Capacity	Neutral salt Splitting Capacity	Moisture content	Exchange Capacity	Neutral salt Splitting Capacity	Moisture content
h	meq/g	meq/g	%	meq/g	meq/g	%	meq/g	meq/g	%
0	5.35	4.65	63.0	4.80	4.40	42.2	2.69	2.53	23.5
6	5.64	4.60	64.0	4.79	4.30	42.5	2.92	2.80	24.2
13	6.11	4.55	65.5	4.85	4.45	43.3	—	—	—
60	8.25	4.50	78.5	5.40	4.30	47.5	3.24	2.85	25.5
109	8.12	—	89.0	6.16	4.25	62.5	4.06	3.10	31.0

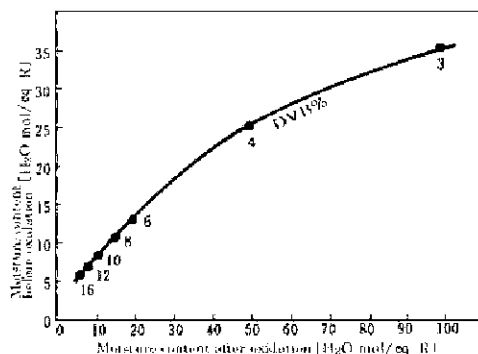
Figure I-4-4 demonstrates the moisture content changes of SACERs of different crosslinkages, DIAION® SK-series, in oxidation by long-time dipping in H_2O_2 solution; the moisture content are indicated in moles per the neutral salt splitting capacity. This Figure shows that low crosslinkage IERs tend to increase the moisture content and to swell irreversibly.

Long-term use of SACERs makes them swell gradually and irreversibly. It is necessary to choose high crosslinkage IERs when they are used in the conditions where some oxidation occurs or when the used IERs have already swollen irreversibly much.

We have already explained that polystyrenesulfonic acid (PSA) solve from SACERs' structures through oxidation process. PSA is captured by AERs as organic contaminants. However, the capacity to capture PSA is

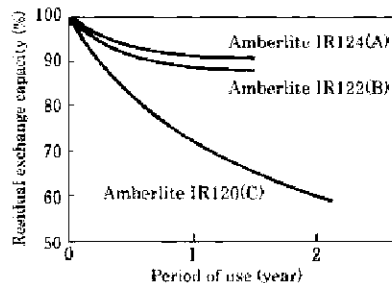
limited to a very little level, thus PSA usually leaks into the effluent soon after AERs lose such capacity and makes the effluent quality worse.

To observe the increase of moisture content of IERs helps us to decide whether they are oxidized much or not.



[Fig. I-4-4] Oxidation of SACERs of different crosslinkages with 30% H₂O₂

In order to protect IERs from such oxidation when the influents contains oxidizing compounds such as free chlorine, they should be removed by the pre-treatment with active carbons or by addition of reducing agents, e.g. Na₂SO₃. The oxidation is affected not only by such oxidizing compounds contents but also by temperatures, pH and heavy metal contents. Thus, though it is difficult to control the oxidation by the oxidizing contents only, some control criteria are set as in Table I-4-3.



[Fig. I-4-5] Crosslinkage vs. Oxidative degradation⁽¹²⁾
[Crosslinkage order: A > B > C, whereas IER C is of the standard crosslinkage]

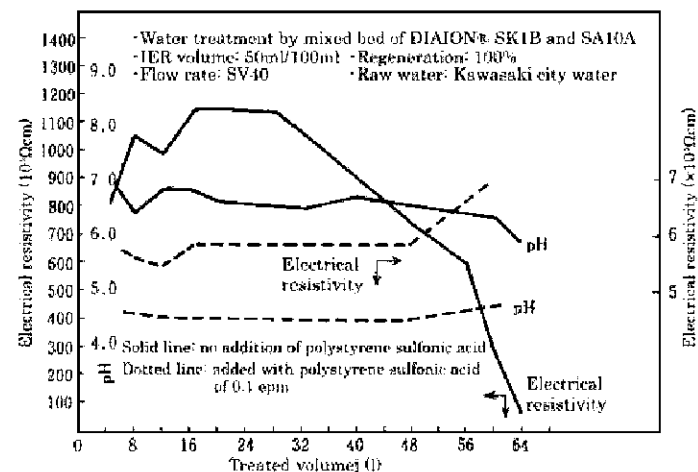
[Table I-4-3] Tolerance of DIAION® SK1B against Cl₂

Temperature (°C)	Cl ₂ Tolerance (mg/l)
5~10	0.6
10~15	0.4
15~20	0.2
20~25	0.1

We will explain again that low crosslinkage IERs tend to be oxidized and to swell irreversibly, refer to Fig. I-4-5, and that further swelling due to oxidation brings large pressure drops and the dissolution of PSA, the component of IER matrix. PSA is too large in its molecular size to diffuse in the inside of IERs and to be captured enough by the AER column next to the CER column, and it leaks into the effluent.

In the two-bed with two-column or two-bed with three column systems, Na⁺ that leaks from CERs neutralizes PSA and thus pH drops rarely occur. In the mixed bed system, on the contrary, pH drops sometimes occur. Figure I-4-6 exemplifies the effluents qualities with and without the addition of the eluting compounds from SACERs through oxidation. High crosslinkage IERs are recommended to treat the influents with oxidizing contaminants.

High crosslinked IERs are, of course, oxidized similarly as crosslinkage ones, but it takes long to swell. This is one advantages of high crosslinked IERs, refer to Figure I-4-5.



[Fig. I-4-6] Effects on effluent quality by Polystyrenesulfonic acid

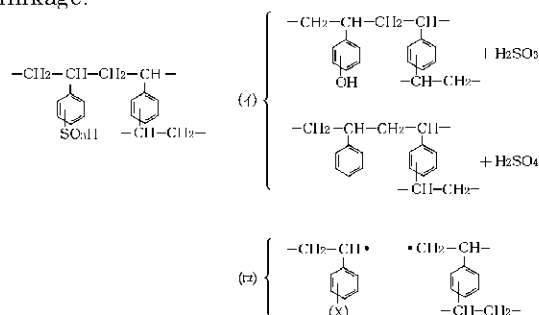
(4) Thermal decomposition of SACERs

SACERs are relatively thermally-stable due to their chemical structures, crosslinked copolymers of styrene and divinylbenzene with sulfonic acid groups. However with long terms over some temperature, the decomposition slowly commences with the dropping-outs of the ion-exchange groups and then with the breaking-ups of the matrices.

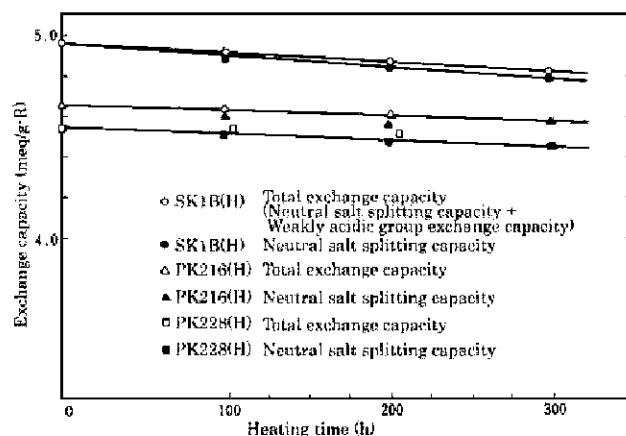
Figure I-4-7 illustrates such mechanism of the thermal decomposition.

The decline of the ion-exchange capacity of SACERs by their thermal decomposition is summarized in Fig.I-4-8 (H-form IER at 120 °C), in Fig.I-4-9 (H-form, 150 °C) and in Fig.I-4-10 (Na-for, 150 °C). The effect of crosslinkages on thermal decompositions and the formation of phenol groups through thermal decomposition are shown in Fig.I-4-11 and in Fig.I-4-12.

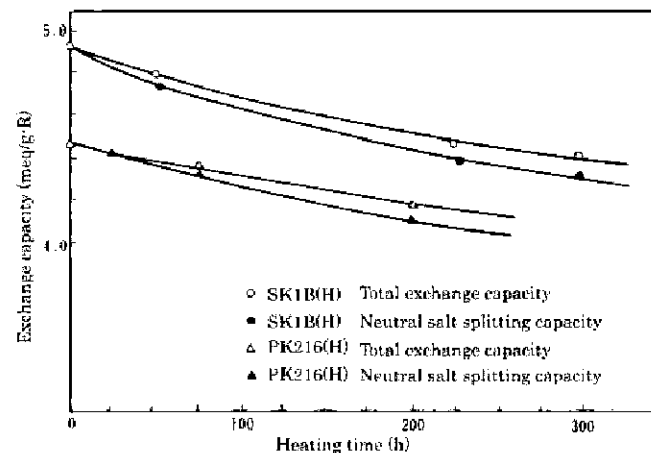
These Figures let us know that low crosslinkage and H-form IERs are thermally superior to high and salt-form ones respectively. The thermal stability of gel-type IERs are almost the same as porous-type ones of a similar crosslinkage.



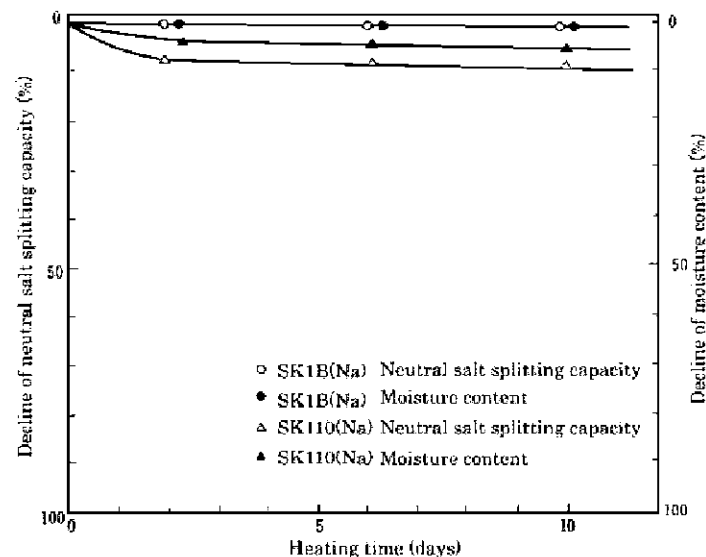
[Fig.I-4-7] Thermal decomposition mechanism of SACERs



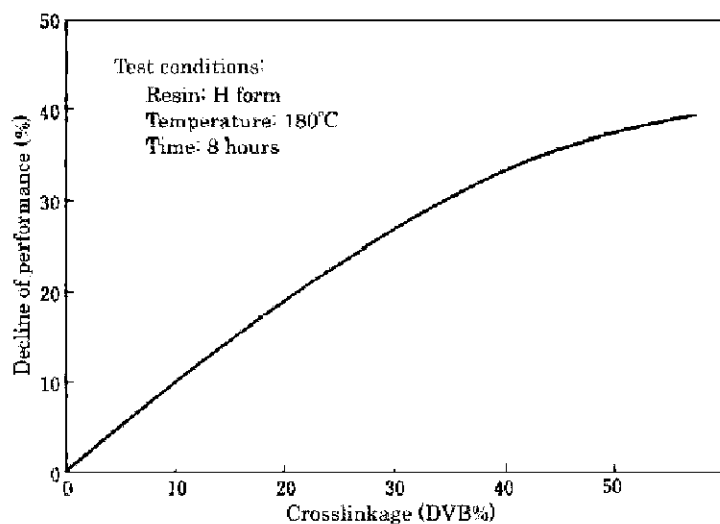
[Fig.I-4-8] Decline of Exchange Capacity caused by Thermal Decomposition of SACERs (120 °C)



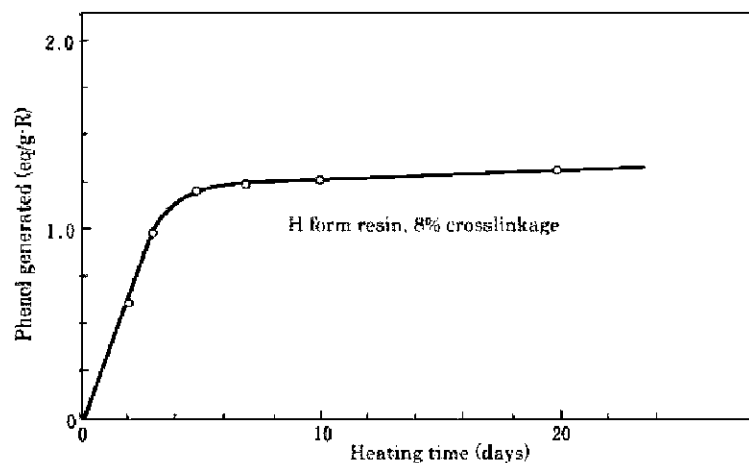
[Fig.I-4-9] Decline of Exchange Capacity caused by Thermal Decomposition of SACERs (150 °C)



[Fig.I-4-10] Decline of Exchange Capacity caused by Thermal Decomposition of SACERs (150 °C)



[Fig.I-4-11] Effect on Efficiency Declines caused by Thermal Decomposition of SACERs



[Fig.I-4-12] Formation of Phenol groups by Thermal Decomposition of SACERs (180°C)

To sum up is as follows:

1. The IERs in H-form, regenerated form, of the standard crosslinkage, e.g. SK1B and PK216, are thermally stable and can be in use for considerably long hours at over 120°C. Both high and low crosslinkage IERs are, at 150°C, unstable with large efficiency declines.
2. The IERs in Na-form, loaded form, are stable at 120°C and can be in use for considerably long hours at 150°C, but unstable with large efficiency declines at 180°C.

The results mentioned above are based on the rather short-period experiments shorter than the practical operations. Thus, thorough and longer period examinations are recommended for the actual use at high temperatures.

(5) Oxidation of SBAERs

In accordance with lowering functional groups, with lowering basicity, decrease the moisture content, the degree of swelling, the total exchange capacity and the neutral salt splitting capacity and increase the exchange capacity of weakly basic groups.

Dropping-outs of the exchange groups decrease the reaction rates and increase ion-leakages.

Lowering basicity decreases the exchange capacity toward weakly acidic components as SiO_2 and HCO_3^- .

Besides oxidized SBAERs lose their ion-exchange capacities through the basicity decrease and the dropping-outs of the functional groups, their own polymer matrices are oxidized at the same time.

Low crosslinkage IERs are easily oxidized in this way. Tables I-4-4 and I-4-5 summarize the results of both types, I and II, of SBAERs of different crosslinkages oxidized in severe conditions. The results are the exchange capacities and moisture contents before and after the dipping for 75 days in NaClO solutions and the oxidation. Though this experimental condition is very severe in comparison with the practical fields, but these results suggest that low crosslinkage SBAERs tend to lose the neutral salt splitting capacity and to be oxidized easily and that the type I is easier to be oxidized than type II.

[Table I-4-4] Oxidation by NaClO of SBAERs (type I) of different crosslinkages

DVB %	Before Oxidation		After Oxidation			
	Moisture content	Neutral salt Splitting Capacity (ca.10 ml)	Moisture content	Neutral salt Splitting Capacity	Exchange Capacity of Weakly basic groups	Total Exchange Capacity
	%	meq	%	meq	meq	meq
2	70.87	6.8	89.12	0.05	1.64	1.69
4	59.46	10.6	73.52	1.05	2.96	4.01
6	48.08	12.6	52.76	1.65	3.20	4.85
7	47.78	13.4	49.04	2.33	4.10	6.43
8	44.44	13.4	45.20	2.45	4.14	6.59

[Table I-4-5] Oxidation by NaClO of SBAERs (type II) of different crosslinkages

DVB %	Before Oxidation		After Oxidation			
	Moisture content	Neutral salt Splitting Capacity (ca.10 ml)	Moisture content	Neutral salt Splitting Capacity	Exchange Capacity of Weakly basic groups	Total Exchange Capacity
	%	meq	%	meq	meq	meq
2	70.52	7.4	37.75	0.01	3.60	3.61
4	55.31	10.6	36.89	0.03	5.16	5.19
6	45.69	12.7	33.84	0.15	6.04	6.19
7	43.12	13.5	33.40	0.38	5.88	6.26
8	39.82	13.3	30.03	0.36	5.88	6.24

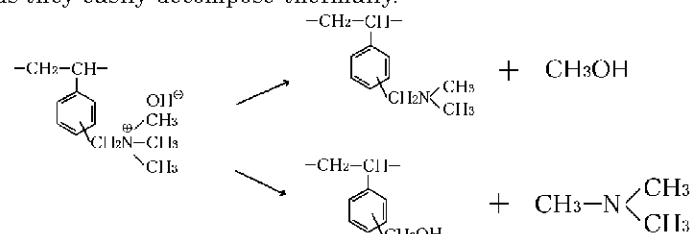
When one use SBAERs in some oxidative conditions, one should choose the high crosslinkage SBAERs. Such SBAERs should be used when there are possibilities that the neutral salt splitting capacities decline to a large extent due to oxidations. However, since the decomposition of the ion-exchange groups and the organic contaminants cause the decline of the neutral salt splitting capacity, it is not decided that the SBAERs are really oxidized based on the decline of the neutral salt splitting capacity only. The moisture contents generally tend to decrease due to the lowering basicity of the strong basic exchange groups, and Table I-4-4 shows that the moisture content increase after the oxidation of SBAERs. One should conclude that the SBAERs are oxidized when both the lowering basicity of the exchange groups and the moisture content increase are both observed.

(6) Decomposition of the functional groups of AERs

Most of the ion-exchange functional groups of AERs are quaternary ammonium groups or amine groups and are easy to be decomposed chemically. These chemical decompositions are classified into thermal decomposition and oxidative one.

1) Thermal decomposition

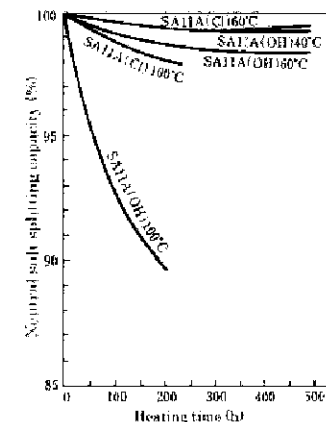
SBAERs have quaternary ammonium groups as ion-exchange groups and thus they easily decompose thermally.



[Fig. I-4-13] Schemes of thermal decomposition of SBAERs

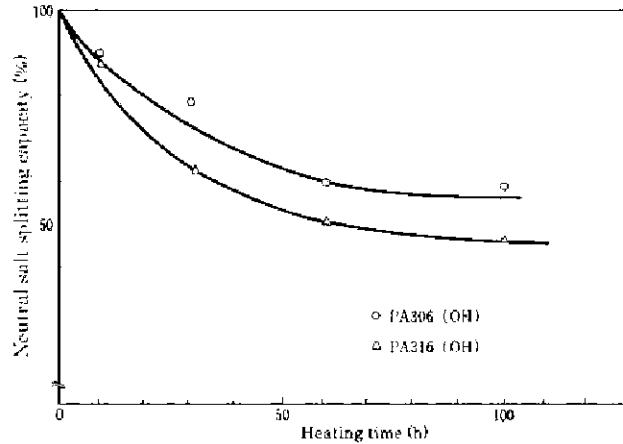
As is illustrated in Figure I-4-13 the scheme of the thermal decomposition of SBAERs, this decomposition is initiated by its own self-decomposition. When such SBAERs are in OH-form, in particular, the decomposition is accelerated due to the attack to the C-N bonds in quaternary ammonium groups by highly nucleophilic OH ions. Such decompositions decrease IERs' exchange capacity and basicity. The typical by-products of this decomposition are methanol and trimethylamine from type I IERs and methanol, ethylene glycol, dioxane and diethanolamine from type II IERs.

Figures I-4-14 through I-4-16 illustrate the declines of the exchange capacities of two kinds of IERs, type I and II, when they are heated for a long time. The neutral salt splitting capacities of both types of IERs decline with prolonged heating times. Type II is less thermally stable than type I. Figure I-4-17

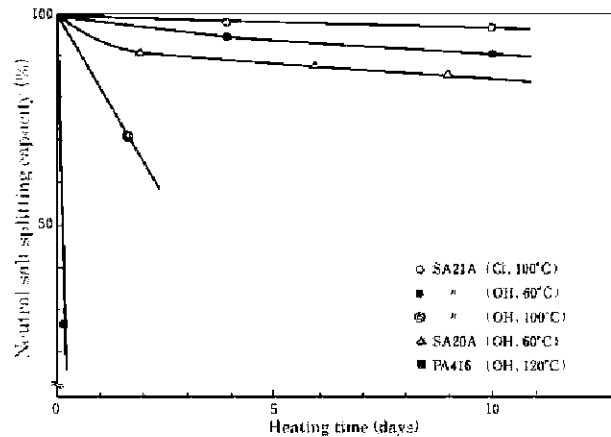


[Fig. I-4-14] Decline of Exchange Capacity caused by thermal decomposition: Strong basic Anion Exchange Resin type I (SA11A)

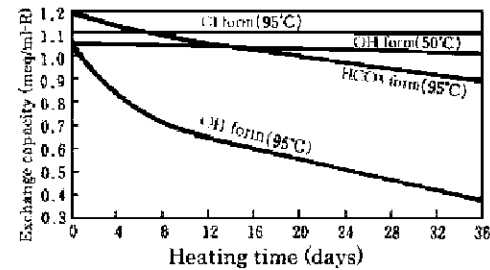
shows such declines of the exchange capacities of three different forms of type II IERs: Cl-form, HCO₃-form and OH-form. It explains that OH-form decompose its exchange capacity drops very rapidly.



[Fig.I-4-15] Decline of Exchange Capacity caused by thermal decomposition: Strong basic Anion Exchange Resin type I (120°C)

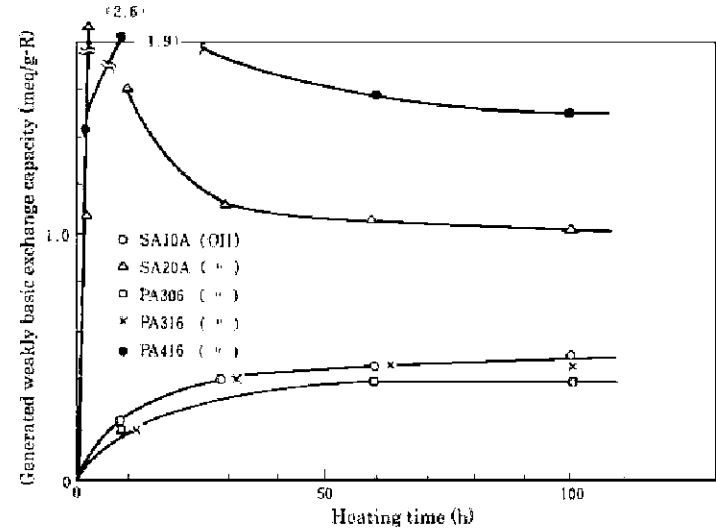


[Fig.I-4-16] Decline of Exchange Capacity caused by thermal decomposition: Strong basic Anion Exchange Resin type II



[Fig.I-4-17] Decline of Exchange Capacity of Dowex® 2 (corresponding to DIAION® SA20A) (13)

Figure I-4-18 illustrates the trends of generation of weakly basic groups caused by the thermal decomposition of SCAERs.



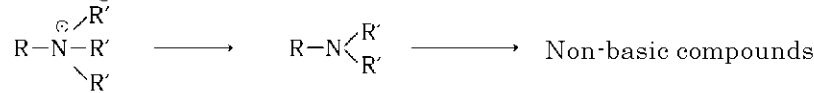
[Fig.I-4-18] Weakly basic groups generated by thermal decomposition of SBAERs (120°C)

Since SBAERs in OH-form, a regenerated form, are easily decomposed thermally, as we have explained above, treating hot influents accelerate the deterioration of SBAERs. The maximum operating temperatures of SBAERs listed in the IERs catalogue are the practical limit temperatures and they do not mean there never occurs thermal decomposition below these temperatures: e.g. OH-form of type I is 60°C, Cl-form of type I is 80°C, OH-form of type II is 40°C, Cl-form of type I is 60°C. Furthermore,

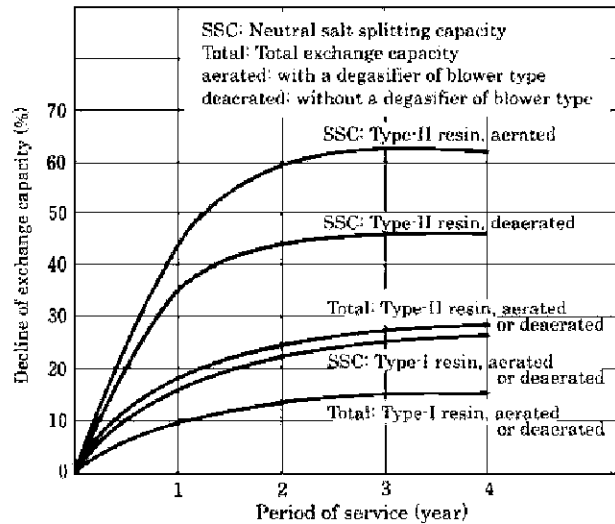
OH-form SBAERs tend to be decomposed even at normal temperatures so one should not hold SBAERs in OH-form for a long period.

2) Oxidative decomposition

The ion-exchange groups of AERs (Anion Exchange Resins) are quaternary ammonium groups or amine ones, and such groups are easily decomposed oxidatively by dissolved oxygen in influents. The resin matrices of AERs are also oxidized in the same way we previously explained about SACERs. Because of such oxidation, the basicity of functional groups become weak and some functional groups drop out from the resin matrix. The resin matrices sometimes break and the crosslinkage as IERs declines as a result.



Type II SBAERs tend to degrade in their own performance thermally or by oxidation, and the neutral salt splitting capacity sometimes decreases by around 40% in a year. Hence, operations at high temperatures should be avoided. Fig.I-4-19 expresses such performance degradation of Type I and Type II IERs.



[Fig.I-4-19] Deterioration of IERs type I & II for long-time use⁽¹⁴⁾

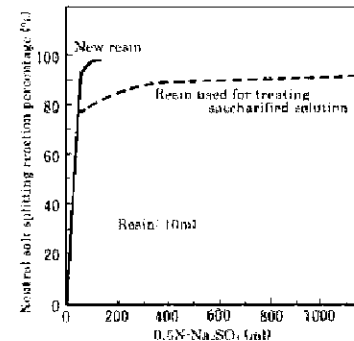
(7) Organic contamination of AERs

Organic contaminants are from humus, synthetic detergents, such as ABS and LBS, in sewerages, and lignin sulfonic acids and high molecular coagulants in wastewaters from pulp industries.

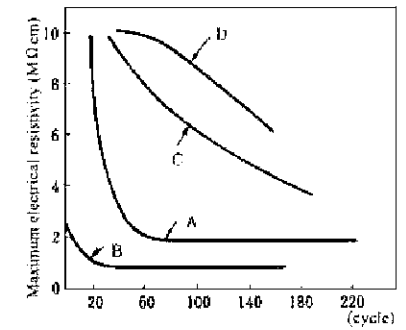
Ion exchange reaction rate, total exchange capacity and neutral salt splitting capacity decrease.

Efficiency of flow and washing declines and worse effluent quality caused by formation of weakly acidic groups.

Organic contaminants in water treatments are from humus, synthetic detergents, such as ABS and LBS, in sewerages, and lignin sulfonic acids and high molecular coagulants in wastewaters from pulp industries. Due to the organic contamination, the ion exchange reaction rate, the total exchange capacity and the neutral salt splitting capacity decrease. The efficiency of flow and washing declines and the effluent quality become worse caused by the formation of weakly acidic groups.



[Fig.I-4-20] Neutral salt splitting reaction percentage of SBAERs



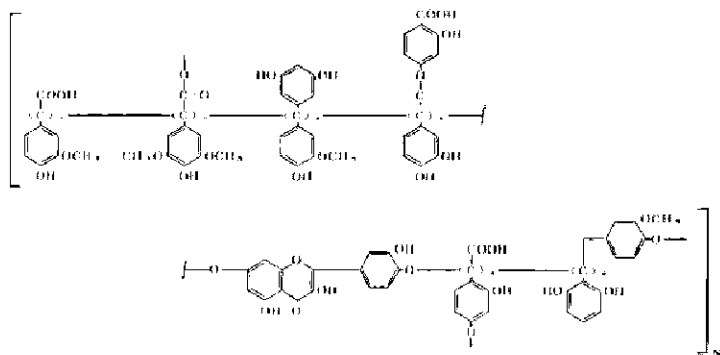
[Fig.I-4-21] Deterioration of SBAERs by Organic contamination

- A: Mixed Bed Demineralizer with Amb.IR120 & Amb.IRA400
- B: Mixed Bed Demineralizer with Amb.IR120 & Amb.IRA410
- C: Mixed Bed Demineralizer with Amb.IR120 & Amb.IRA401
- D: Amb.IRA401(Cl-form) + System A

In water treatments with SBAERs, the effluent quality sometimes deteriorates suddenly after lots of treatment-cycles. Or, sudden black discoloration of IERs and extremely drop in reaction rates are encountered in the treatments of starch sugar or sucrose. Figure I-4-20 illustrates such reaction rate drop and compares the Type II low crosslinkage resin used in starch sugar treatments and the new one. Both resins were subjected to complete regeneration and rinsed and then 1/2N- Na_2SO_4 solution passed through them at the same flow rate. The neutral salt splitting capacity was observed by the titration of NaOH in the both effluents. Whereas the new IERs are fully exchanged with only 200 mL of NaOH solution, the IERs used in starch sugar treatments are not exchanged fully even with 1200 ml of NaOH solution.

Such phenomena are the results of the organic contaminations: that is, SBAERs adsorb organic compounds irreversibly and the micropores are blockaded. The organic contaminants sometimes polymerize after a long time depending on the pH, thus their rejuvenation is difficult.

Similar organic contamination is encountered in water treatments and humus is one of the contaminants in these cases. Fig. I-4-21 exemplifies one example. The curves A and B in this Figure display the decline of effluent quality in accordance with the treatment-cycle increase in the mixed bed demineralization system with Type I or II IERs; compatible to DIAION® SA10A or SA20A, respectively. The curve C is with a low crosslinkage Type I AER of Cl form, compatible to DIAION® SA11A, and the curve D is with Type I IER and a low crosslinkage Type I AER of Cl form, compatible to DIAION® SA10A, as the upper column. The effluent quality of C and D are better than of A and B. This means that the low crosslinkage IERs are resistant to organic contamination.

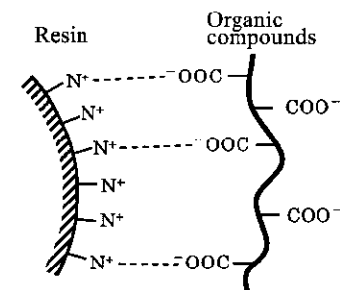


[Fig.I-4-22] Estimated structures of the organic compounds in the effluents⁽¹⁵⁾

Organic contaminated IERs recover their performance to some extent by rinsing them with hot NaCl or HCl solutions, but such recovery is ordinarily unsatisfactory. Another method to recover is dissolution of such contaminants by oxidation with NaClO for example. Care should be taken since the resin matrix is naturally oxidized.

The organic compounds in natural waters, humic acid, fulvic acid and humatmelanic acid, are derived from rotten plants and called humin or humus. All of the chemical structures are not clear yet; one example is illustrated in Fig.I-4-22⁽¹⁵⁾. These organic compounds are too large in size to diffuse into the inside of AERs, but many existing carboxylic groups per molecule of humin ion-exchange with the functional groups at the IERs surface and are captured by IERs. Since those captured by IERs in this way are difficult to be desorbed from IERs by regenerants, the IERs are contaminated consequently.

Once IERs are contaminated enough, the contaminant organic compounds begin to leak without adsorption. This phenomenon is similar to the generation of polystyrenesulfonic acid caused by oxidation of SACERs. Thus, the pretreatment of influents with organic contaminants by activated carbon is recommended to keep the lifetime of IERs long enough. Porous type IERs are superior to gel type in this case, but they are, of course, contaminated. The pretreatment of influents are recommended when porous type IERs are used.



[Fig. I-4-23] Schema of adsorption of humic substances by AERs

Once IERs are contaminated with organic compounds, free carboxylic groups of organic compounds play the roles of weakly acidic functional groups. That is to say, they are ion-exchanged by NaOH, a regenerant, and cause Na leakage during the rinse or loading.